1-1-2013

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Abstract

This study develops a novel method to remove the free cations created during the synthesis of ionic liquid. The cations are removed from the ionic liquid by size-selective adsorption onto chemically surface-modified Zeolite. The porous crystal nano-structure of Zeolite has several electron-rich Al sites to attract cations. While large cations of an ionic liquid cannot access the Zeolite nano-structure, small cations like Na+ have ready access and are adsorbed. This study confirms that: Na+ can be removed from ionic liquid effectively using Zeolite; and, in contrast to the conventional and extensively applied ion exchange resin method or solvent extraction methods, this can be done without changing the nature of the ionic liquid.

Keywords

electrolyte, manufacture, quality, zeolite, high, liquids, removal, na+, ionic

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Cho, W., Seo, Y., Jung, S. Jae., Lee, W. Gil., Kim, B. Chul., Mathieson, G. & Yu, K. (2013). Removal of Na+ from Ionic Liquids by Zeolite for High Quality Electrolyte Manufacture. Bulletin of the Korean Chemical Society, 34 (6), 1693-1697.

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http://dx.doi.org/10.5012/bkcs.2013.34.6.1693

Removal of Na^+ from Ionic Liquids by Zeolite for High Quality Electrolyte Manufacture

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Received February 9, 2013, Accepted March 14, 2013

This study develops a novel method to remove the free cations created during the synthesis of ionic liquid. The cations are removed from the ionic liquid by size-selective adsorption onto chemically surface-modified Zeolite. The porous crystal nano-structure of Zeolite has several electron-rich Al sites to attract cations. While large cations of an ionic liquid cannot access the Zeolite nano-structure, small cations like Na^+ have ready access and are adsorbed. This study confirms that: Na^+ can be removed from ionic liquid effectively using Zeolite; and, in contrast to the conventional and extensively applied ion exchange resin method or solvent extraction methods, this can be done without changing the nature of the ionic liquid.

Key Words : Ionic liquids, Purification, 1-Ethyl-3-methylimidazolium tetrafluoroborate, Electrolyte, Zeolite

Introduction

Ionic liquids (ILs) are low-temperature molten salts, that is, liquids composed of ions only. The salts are characterized by weak interactions, owing to the combination of a large cation and a charge-delocalized anion. This results in a low tendency to crystallize due to flexibility and dissymmetry.

The most common cations in use are those containing imidazolium, pyridinium, phosphonium, pyrrolidinium, tetraalkylphosphonium, tetraalkylammonium, and trialkylsulfonium, which can combine with anions such as tetrafluoroborate hexafluorophosphate, trifluorotris(pentafluoroethyl)-phosphate, thiocyanate, dicyanamide, ethyl sulfate, and bis-(trifluoromethylsulfonyl)amide.

Ionic liquids have been investigated as an ion conductive matrix as well as a reaction solvent due to their unique physical properties: a wide liquid temperature range; high ionic conductivity; a wide voltage window; and nonvolatility. Therefore, ILs have attracted much attention as a promising alternative to conventional organic electrolyte and organic solvent systems.[1-6] In particular, IL electrolyte for electro-chemical storage devices like batteries and capacitors can be made by metathesis anion substitution in combination with various organic cations.[1,7] Counter ions remain after the substitution. In a secondary lithium-ion battery, residual Li^+ is not detrimental to battery performance. However when cheaper Na^+ is used for electrolyte synthesis, instead of Li^+, residual Na^+ competes with Li^+ ions during battery usage. This reduces the electrode reaction effectiveness. Elimination of residual Na^+ ion is crucial.

A purification process that eliminates Na^+ ion and its counter ion Br^- can solve such problems. Physical purification methods are being studied extensively. Solvent extraction, adsorption, crystallization and membrane technologies have attracted many researchers. However, it has been revealed that those methods cause color changes or IL decomposition.[8-11] It appears that by established techniques, counter ions with same ionicity are unnecessarily removed, affecting the resulting ionic liquid's performance. A novel method to purify ILs without changing them is in great demand.

Zeolite has nanopores of about 3-10 diameter and surface area of about 100-1000 m^2g^{-1}. The corresponding crystallographic structure is formed by adjacent tetrahedra of AlO_4 and SiO_4. These tetrahedra are the basic building blocks for various Zeolite structures, such as ZSM-5, zeolite-X, zeolite-Y and zeolite-L *etc*. Due to the presence of alumina, Zeolites exhibit negatively charged pore edges, which are counter-balanced by positive cations such as K^+ or Na^+ resulting in a strong electrostatic field at the pore surface. By chemically modifying pore surfaces, Zeolite can be given specialized functions, such as: ion exchange; dehydration; molecular adsorption catalyst; mineral remover; and so on.[12]

In this paper, a novel purification approach to eliminate counter ions produced during the synthesis of ILs, without color change or chemical decomposition, is developed. We synthesized IL and specially modified the surface of Zeolite to a particular form. This was followed by investigation of the purification performance for elimination of Na^+ ion in ILs. For comparative studies, ion exchange or solvent extraction were also applied. We found that ILs purified by Zeolite are remarkably effective as electrolyte for use in energy storage or conversion devices

Experimental

Materials and Equipment. 1-Methylimidazole, bromoethane, sodium tetrafluoroborate, methanol(anhydrous 99.8 %), acetonitrile(anhydrous 99.8%), sodium Y-zeolite, ammonium chloride, aluminum oxide, Dowex® 50W8 and all the

other chemical reagents were purchased form Sigma-Aldrich Co. and used without any further purification. Ionic liquid sample for the purification test, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4) was prepared by direct synthesis.

The structure of the synthesized ionic liquid was analyzed using a Varian Gemini-200 series NMR spectrophotometer. The structural changes of Zeolite used for [EMIM]BF_4 purification was evaluated by FT-IR (Varian 1000 FT-IR Scimitar series) and XRD (Rigaku XRD, λ = 1.5418 Å, 298 K). Na^+ residuals in the refined samples were analyzed using the Orion 720A ion counter with ISTEK sodium electrode. Ionic liquid decomposition in samples purified by the three different treatment methods were measured by using UV-Vis spectrophotometry (Varian Cary 50 Conc.) in the absorption range of 290 nm to 600 nm. Ionic conductivities were measured by WTW's COND 3110 Conductivity Meter using Tetracon 325 electrodes with temperature compensation.

Preparation of Surface Modified Zeolite. Surface modified Zeolite was prepared from NaY-zeolite by room temperature chemical treatment with NH_4Cl to produce NH_4Y-zeolite. Firstly, 20 g of NaY-zeolite was mixed with 200 mL 2 N NH_4Cl for 24 h then residual NH_4Cl solution was removed by filtration and washing with distilled water. The modification and cleaning procedure was repeated twice. Final washing continued until low residual was confirmed by nil precipitation in filtrate reacted with $AgNO_3$ solution. The produced NH_4Y-zeolite sample was collected and dried in an oven at 100 °C for 24 h, then calcined in an electric furnace at 450 °C in normal atmosphere for 6 h. The crystalline phase of the produced zeolite, as well as any structural changes, was identified by analysis of FT-IR and XRD spectra.[13,14]

Purification of [EMIM]BF_4. Particulate impurities in the [EMIM]BF_4 samples were removed using a 0.45 μm PTFE membrane filter. Then samples were dried in an oven at 100 °C for 24 h. The Na^+ residual, prior to attempted Na^+ removal, was measured by Na^+ ion counter.

Purification by Surface Modified Zeolite. Purification of [EMIM]BF_4 was performed using surface modified zeolite as follows. 10 g [EMIM]BF_4 was mixed with 1 g surface modified Zeolite for 24 h at room temperature. The Zeolite was removed using 0.45 μm PTFE membrane filters. Then collected [EMIM]BF_4 was dried in a vacuum oven under high vacuum at 100 °C for 24 h. Residual Na^+ after purification completion was measured using the Na^+ ion counter. Potential IL degeneration due to treatment, by surface modified Zeolite and other treatment methods, was measured by recorded UV-Vis spectra in the 290 nm to 600 nm range. Then ionic conductivity was checked with a conductivity meter with two carbon electrodes. Comparison experiments were carried out using standard industrial purification methods: ion exchange resin; and solvent-to-solvent extraction.

Ion Exchange Resin Method. Dowex®50W8 cationic ion-exchanger resin was used. The ion exchange resin was pretreated with 0.1 N HCl solution and 0.1 N NH_4Cl solution, and then washed with anhydrous methanol. Pretreated resin was packed into a 5 cm I.D. glass column and the unrefined [EMIM]BF_4 sample was passed through at 1 $mLmin^{-1}$. Residual Na^+ was measured using the Na^+ ion counter.

Solvent to Solvent Method. The solvent-to-solvent extraction method is a commercialized process using organic solvent, intended to remove only residual Na^+ ion from the mixture of IL and Na^+ ion. In this study Na^+ ion extraction from the mixture of [EMIM]BF_4 and Na^+ ion in deionized water was carried out with Methylene Chloride (MC) as solvent because it has a good solubility for [EMIM]BF_4 but does not dissolve Na^+.[15]

Because MC is non-polar organic solvent, which has poor water solubility, and MC has density 1.33 times that of H_2O, the two solvents are readily separable. Therefore, we used a solvent-to-solvent extraction apparatus, which enabled ILs to be extracted and concentrated continuously. During the refining process, a small amount of [EMIM]BF_4 is dissolved the MC but Na^+ ions do not dissolve in MC. In this experiment, 20 g of unpurified [EMIM]BF_4 and 40 g H_2O were added to the solvent-to-solvent extraction chamber, then about 200 g MC was added to the extraction chamber and refluxing flask. Then the refluxing flask was operated continuously at 70 °C. [EMIM]BF_4 contained in the MC fraction was removed by evaporation at 70 °C in high vacuum. Residual Na^+ was measured using an Na^+ ion counter.

IL Synthesis. 1-Methylimidazole was mixed with 1-bromoethane at 1:1.2 mole ratio in cold acetonitrile (ACN) and refluxed for 24 h in an ice bath. The solvent ACN and residue were then removed by vacuum evaporation at 70 °C. Then the structure of collected prospective 1-Ethyl-3-methylimidazo-lium bromate ([EMIM]Br) was elucidated using ^{1}H-NMR spectroscopy (Varian Gemini 200NMR) as fellows: 1-Ethyl-3-methylimidazolium bromate ([EMIM]Br); ^{1}H-NMR, 200 MHz (DMSO-d_6) δ 10.55 (s, 1H), 7.44 (s, 2H), 4.42 (q, 2H), 4.13 (s, 3H), 1.62 (t, 3H).

The collected compound was dissolved in acetone and mixed with the $NaBF_4$ anion source. Then metathesizing was performed at room temperature for 24 h with stirring, and a white precipitate of [EMIM]BF_4 was formed. The [EMIM]BF_4 was collected by filtration, followed by washing with ether and concentrated by vacuum evaporation at 70 °C for 24 h, then dried in a vacuum oven at 80 °C for 24 h. After that, the sample was moderately purified using Al_2O_3 in ACN to remove gross inorganic ion residues such as Na^+. The samples were finally collected and the structures were again elucidated using ^{1}H-NMR spectroscopy as follows: 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4). [EMIM]BF_4; ^{1}H-NMR, 200 MHz (DMSO-d_6) δ 8.55 (s, 1H), 7.41 (s, 1H), 7.35 (s, 1H), 4.14 (q, 2H), 3.83 (s, 3H), 1.41 (t, 3H).[16]

Results and Discussion

UV-Vis Spectroscopy of the Synthesized ILs. Figure 1 shows UV-Vis absorption spectra of [EMIM]Br and [EMIM]BF_4 from 290 nm to 600 nm. A strong absorption peak is appears near 320 nm. This is similar to previously reported results.[9,11]

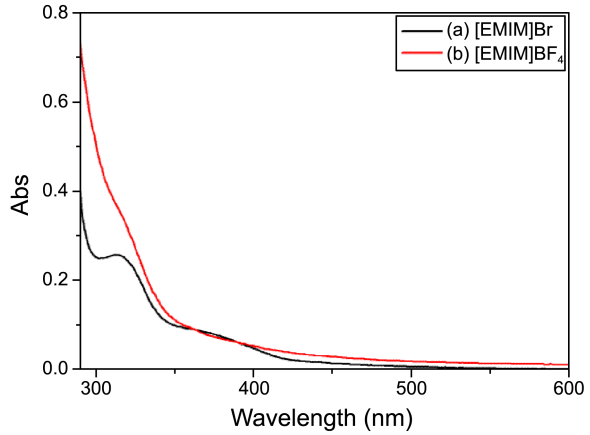

Figure 1. UV-Vis spectra of (a) [EMIM]Br and (b) [EMIM]BF_4.

UV-Vis spectra of [EMIM]Br and [EMIM]BF_4 showed the absorbance is close to zero above 400 nm while increasing to 0.8 at lower wavelengths. The clear or greenish color of the [EMIM]BF_4 is due to short wavelength absorbance. This is also associated with the red shift induced by the effect of counter anions. However, the absorbance bands are mostly due to the resonance structure of the 1-Ethyl-3-methyl-imidazolium cation in [EMIM]BF_4.[17]

IR Spectroscopy of Zeolite. On completion of the Zeolite's surface modification, IR-spectroscopy and XRD were conducted to confirm chemical structure and composition. A shoulder peak in IR spectra in the 900-1000 cm^{-1} range occurs due to elimination of Na^+ and substitution with other ions inside the skeletal structure of Si-O-Si or Si-O-Al.[15,16] Figure 2 shows a shoulder peak in the IR spectrum at 908 cm^{-1} due to residual H^+ ions bound on the zeolite surface after calcination. This represents the character of surface modified Zeolite. The peaks from 1300 cm^{-1} to 500 cm^{-1} confirmed a typical Zeolite spectrum with regular structure, suitable for the purpose of this study.[18-20]

XRD of Zeolite. The reduced peak heights in the calcined modified Zeolite XRD spectrum compared to the NaY-zeolite XRD spectrum, shown in Figure 3, confirmed that surface modification made the Zeolite less crystalline. However, the peak positions for both original and modified

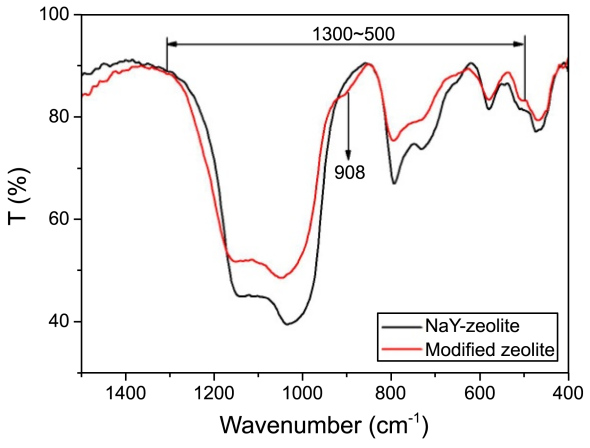

Figure 2. IR-spectra of NaY-zeolite and Modified zeolite.

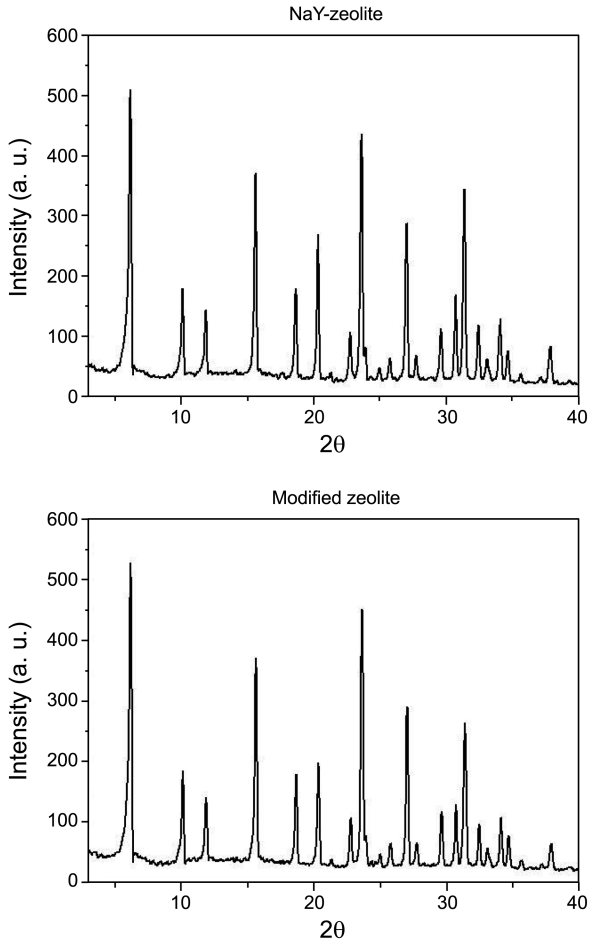

Figure 3. XRD-spectra of NaY-zeolite and Modified zeolite.

zeolite are identical.

These results demonstrated that the zeolite structure was not changed by NH_4Cl treatment followed by calcination at 450 °C.[13]

Purity Evaluation of IL by Ion Exchange Resin. After dissolving [EMIM]BF_4 in methanol, it was passed through the column packed with cation exchange resin and then Na^+ ion concentration in recovered IL was measured. It confirmed a 300 ppm decrease in Na^+ from 9500 ppm in unpurified IL and a 30% reduction in volume. This result indicates that ion exchange resin is not suitable as it is in effective and causes loss, probably due to IL adsorption by resin.

Purity Evaluation of IL by Solvent to Solvent Extraction Method. A 95% elimination of Na^+ ion by solvent-to-solvent extraction, from 9500 ppm to 490 ppm in MC solvent, was measured.

Purity Evaluation of IL by Surface Modified Zeolite Treatment. Modified zeolite has the maximum capacity for absorption of Na^+ ions. Purification of [EMIM]BF_4 was conducted using Zeolite modified to the Modified zeolite type. The Na^+ ion concentration in [EMIM]BF_4 was reduced from 9500 ppm to 570 ppm, 94% reduction. The molecular structure of [EMIM]BF_4, identified using ^{1}H-NMR spectra, was the same before and after purification. No significant IL volume change was measured, indicating that there was no

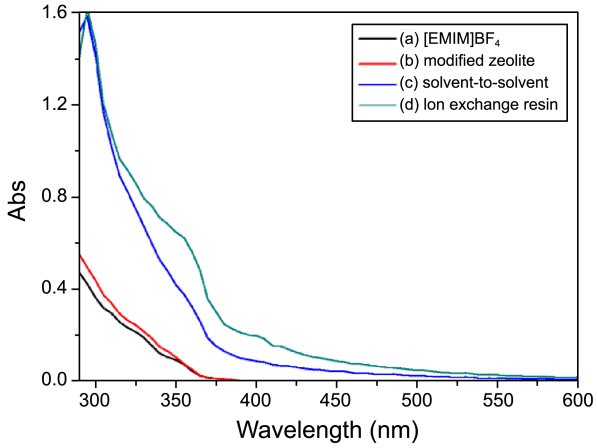

Figure 4. UV-Vis Spectra of $[EMIM]BF_4$ as a function of purification method (a) $[EMIM]BF_4$, (b) modified Zeolite, (c) solvent-to-solvent extraction and (d) ion exchange resin.

absorption of IL cations onto the surface of Modified zeolite.

Comparative Studies by UV-Vis Spectroscopy and Ionic Conductivity. Pure 1-alkyl-3-imidazolium bromate ionic liquids are colorless and transparent but trace impurities impart a yellowish or brown color.[9] UV-Vis spectroscopy is very sensitive to these chromophores and can detect even very slight changes in composition.

UV-Vis absorbance spectrum of $[EMIM]BF_4$ obtained after purification by ion exchange resin showed an increase above 400 nm; the overall baseline rose. Color change to green was observed in the ion exchange treated IL after treatment, consistent with the spectral change. Small and large shoulders appeared at around 400 nm and 370 nm respectively and an absorbance peak appeared at about 200 nm.

Thick yellow precipitates were found to form gradually in ion exchange resin purified IL. This phenomenon is attributed to the impurities produced by decomposition of BF_4 disengaged from IL.[21] The ion exchange resin poorly adsorbs Na^+ ions and combines with imidazolium. It was reported by Nockemann *et al.* that shoulders around 300 nm indicated the existence of impurity and excess anions remaining in imidazolium-based ILs.[9]

UV-Vis spectra of $[EMIM]BF_4$ obtained before and after the purification process by solvent-to-solvent method were consistent with the color change of $[EMIM]BF_4$ from transparent to greenish, due to the partial decomposition of $[EMIM]BF_4$ at the elevated temperature used to remove methylene chloride solvent.

In contrast, purification by modified zeolite did not observably alter the $[EMIM]BF_4$. The UV-Vis spectra of $[EMIM]BF_4$ and $[EMIM]BF_4$ purified by modified zeolite were identical over the entire measured wavelength range. Modified zeolite selectively removed Na^+ ions without removing or altering the $[EMIM]BF_4$.

The ionic conductivities of $[EMIM]BF_4$ purified by three different methods are shown in Table 1. Ionic conductivity of the $[EMIM]BF_4$ before purification was 10.0 $mScm^{-1}$. Table 1 shows that Modified zeolite purified $[EMIM]BF_4$ had a measured conductivity of 12.90 $mScm^{-1}$, higher than that of the samples purified by ion exchange resin, 11.50 $mScm^{-1}$ or by solvent-to-solvent extraction, 12.10 $mScm^{-1}$. The Modified zeolite purification method produces an $[EMIM]BF_4$ product that is potentially superior for electrochemical energy storage and conversion purposes.

Table 1. Residual $[Na^+]$ in $[EMIM]BF_4$ purified by ion exchange, solvent-to-solvent extraction, and modified Zeolite

	Ion exchange resin	Solvent-to-solvent extraction	**Modified Zeolite**
Before Purification (ppm)	9500	9500	**9500**
After Purification (ppm)	9200 ± 81.6	490 ± 12.2	**570 ± 16.3**
Efficiency (%)	3.2	95	**94**
Reduction in IL Volume (%)	30 ± 1.63	23 ± 0.82	**3 ± 0.16**
Ionic conductivity ($mS\ cm^{-1}$)	11.5 ± 0.163	12.1 ± 0.245	**12.9 ± 0.082**

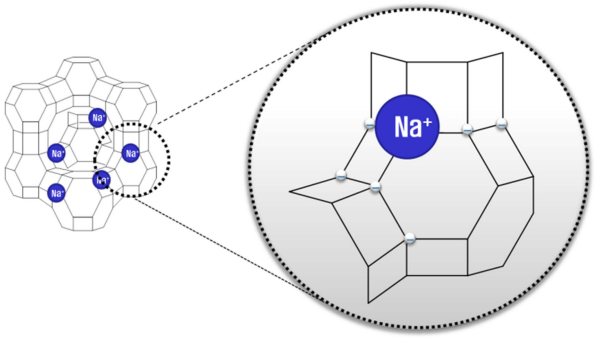

Figure 5. The structure of zeolite showing Na^+ adsorption at anion sites on inner ring edges.

Mechanism of Modified Zeolite Purification. It is thought that highly purified $[EMIM]BF_4$ can be obtained by modified zeolite treatment because the zeolite nano-pores size-restrict access to the negatively charged Al sites that are inside ring structures,[22] shown in Figure 5. Hence, large organic cations are not absorbed but Na^+ ion is absorbed.

Conclusion

We have demonstrated that a proton exchanged Y-zeolite can remove Na^+ ions from the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate($[EMIM]BF_4$). The modified zeolite is prepared from NaY-zeolite by exchanging Na^+ with NH_4^+ followed by calcination. In comparison to traditional methods for ionic liquid purification, the modified zeolite method is superior because: it achieves about 94% Na^+ removal without adversely affecting the ionic liquid, whereas ion exchange resin achieves relatively poor Na^+ removal and both ion-exchange resins and solvent-to-solvent extraction cause ionic liquid degradation; and $[EMIM]BF_4$ purified by modified zeolite has the highest electrical conductivity. Purifying $[EMIM]BF_4$ with modified zeolite is

potentially a low-cost step in manufacture of high quality electrolyte.

Acknowledgments. This work was funded by the Korean government's National Research Foundation of Korea (NRF) grant MEST S-2012-A0004-00080 and Dongguk University-Seoul.

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